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A polyamidoamine dendrimer as a selective colorimetric and ratiometric fluorescent sensor for Li^+ cations in alkali media

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ABSTRACT

In a DMF + NaOH medium, a polyamidoamine dendrimer having sixteen 1,8-naphthalimide fragments in its periphery, formed a complex only with Li^+ ions, detected by a colour change from red to yellow and by a significant increase in fluorescence intensity. The dendrimer can be used as a selective sensor for Li^+ ions in the presence of other alkali ions such as Na^+ or K^+.

1. Introduction

Polyamidoamine (PAMAM) dendrimers are hydrophilic, highly branched macromolecules with different functional groups in their core and periphery. They are a new class of commercial dendrimers and have been investigated intensively in the recent years [1–4]. The introduction of fluorescent and photoactive chromophore groups into the main dendrimer macromolecule has been among the recent advancements of the research in dendrimer chemistry [5].

Recently we reported the synthesis and PAMAM functionalized dendrimers possessing 1,8-naphthalimides in the periphery and on the effect of different metal cations on their fluorescence properties in the presence of various metal cations. It has been shown that the dendrimers can act as effective photoinduced electron transfer fluorosensors for these metal cations [6–14].

The ratiometric and fluorescent sensors for different metal cations are very attractive [15–20] devices facilitating naked eye detection of harmful pollutants that allows untrained staff to perform monitoring and maintenance.

Sensors for detecting lithium cations are currently in demand for medical applications as well as for monitoring these cations in the lithium batteries [21–26]. It has been of interest to investigate lithium cations in the presence of other important alkali metal cations such as Na^+, K^+, which coexist with Li^+ at relatively high concentrations. Only a few fluorophores have been used for fluorescence detection of lithium cations, and these do not have good absorption and fluorescence properties in the visible region. They all are based on the coordination with lithium ions in organic solvents. To our knowledge no colorimetric and ratiometric fluorescent sensors for lithium cations have been proposed in the literature.

In this paper we report on the functional properties of a modified PAMAM dendrimer from second generation functionalized in its periphery with 4-hexylamino-1,8-naphthalimide fluorescent units and in the presence of alkali metal cations Li^+, Na^+ and K^+. The results are presented and discussed with regard to future development of fluorescent and ratiometric sensors for Li^+ cations.

2. Experimental part

2.1. Materials and methods

The structure of the modified PAMAM dendrimer with 4-hexylamino-1,8-napthalimide units under study is shown in Scheme 1 [7].

UV–vis spectrophotometric investigations were performed on a Kontron 930 spectrophotometer at concentration of 1×10^{-6} mol l^{-1}. The fluorescence spectra were taken on a JASCO

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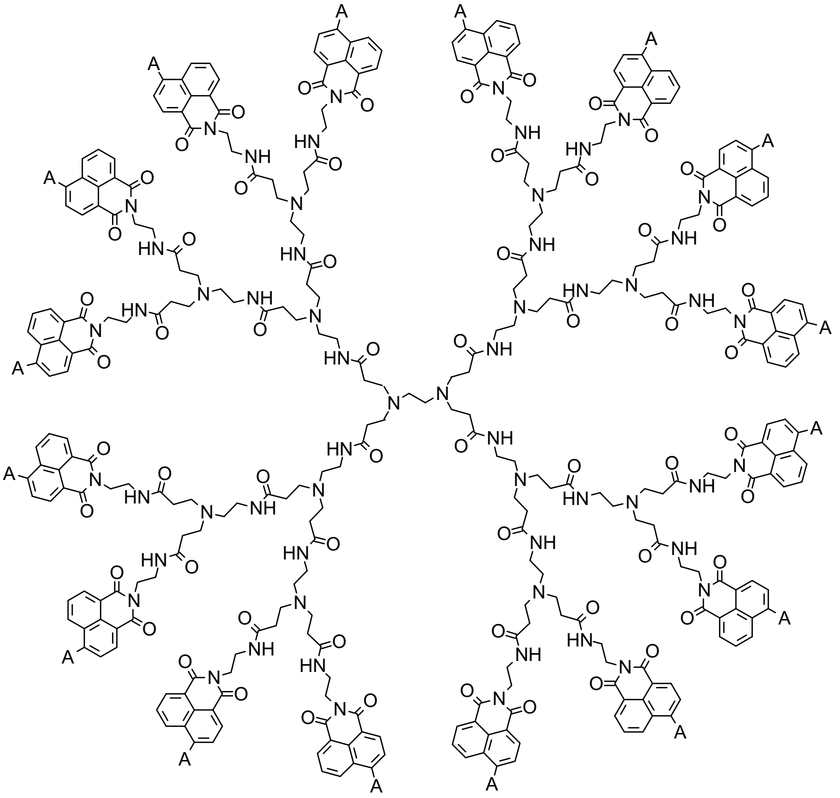

Scheme 1. Chemical structure of second generation PAMAM dendrimer peripherally modified with 4-hexylamino-1,8-naphthalimide.

FP-6500 spectrofluorimeter at the same concentration. *N,N*-Dimethylformamide (DMF) used in this study was of spectroscopic grade. The experimental error was estimated to be 2 nm on the absorption and fluorescence maxima and 5% on the molar extinction coefficient. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra. Fluorescein ($\Phi_F = 0.95$ in 0.1 M NaOH, $\lambda_{Ext} = 439$ nm) and Rhodamine 6G ($\Phi_F = 0.95$ in water, $\lambda_{Ext} = 531$ nm) were used as references. The error on the quantum yield values is estimated to be 5%. The effect of the metal cations (Li^+, Na^+, K^+) upon the absorbance and the fluorescence intensity was examined by adding a few microlitres of stock solution of the metal cations to a known volume of the dendrimer solution (3 ml). The addition was limited to 0.08 ml so that dilution remains insignificant [27]. The effect of the hydroxyl anions on the absorbance and the fluorescence intensity was determined by adding different concentrations of sodium hydroxide (NaOH) to the 3 ml DMF solution of the dendrimer. All spectral measurements in this study were performed at room temperature. $LiNO_3$, $NaNO_3$ and KNO_3 were used as sources of alkali metal cations.

3. Results and discussion

3.1. Photophysical characteristics of the dendrimer in the presence of hydroxyl anions

The influence of hydroxyl anions on functional properties of the dendrimer has been studied in DMF solution with regards to its potential application as a colorimetric and fluorescent sensor for alkali metal cations.

Fig. 1 presents the absorption spectra of the dendrimer in DMF solution in the presence of different concentrations of sodium hydroxide (from 0 to 3×10^{-5} mol l^{-1}). Without sodium hydroxide, the dendrimer absorbs at 439 nm and has an intense yellow colour. Upon titration with different amounts of sodium hydroxide the absorbance at 439 nm is reduced and marked by the appearance of new bands in the ultraviolet region at 335 nm and of another one in the visible region with an absorption maximum at 531 nm, and concomitant formation of the very well-pronounced isosbestic point in the visible region at 474 nm. In this case the colour of the solution is red. The change in the colour and the formation of the new bands at 335 and 531 nm can be explained by a possible deprotonation of the hexylamino substituents at C-4 of the

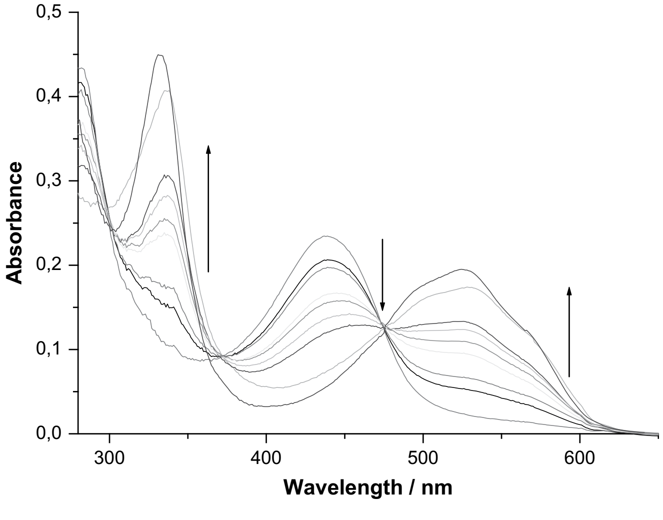

Fig. 1. Absorption spectra of the dendrimer in DMF at different concentrations of NaOH ($c = 0$–3×10^{-5} mol l^{-1}). The concentration of the dendrimer is 1×10^{-6} mol l^{-1}.

1,8-naphthalimide units caused by OH^- anions [28]. That increases the electron density at the nitrogen atom at C-4, hence the respective absorption maximum is bathochromically shifted by 92 nm and the solution changes its colour from yellow to red. Similar results have been reported by Gunnlaugsson et al. [29] and Tian and Liu [30] using $(C_4H_9)_4NF$ as an agent for the deprotonation of the 4-aminosubstituent of the 1,8-naphthalimide fluorophores for detection of F^+.

Fig. 2 shows the fluorescence spectra of the neat dendrimer in DMF solution and in the presence of NaOH (1.6×10^{-5} mol l^{-1}). Without NaOH, the dendrimer emits yellow-green fluorescence with maximum at 524 nm and has quantum yield Φ_F of 0.32 [7]. The fluorescence spectrum of the dendrimer solution in the presence of NaOH shows a broad fluorescence band in the 560–750 nm region with weak red fluorescence emission ($\Phi_F = 0.0006$) and a maximum at 612 nm (Fig. 2). In this case the quantum yield is very low. The results are in good agreement with those reported recently for a bis-1,8-naphthalimide as a fluorophore [28]. This allows the assumption that 1,8-naphthalimide derivatives have great prospects as naked eye sensors for wide range of hydroxyl ions in DMF solution.

3.2. Influence of alkali metal cations on the photophysical properties of the dendrimer in DMF solution

The spectral characteristics of the dendrimer as a colorimetric and fluorescent sensor for three important alkali metal cations (Li^+, Na^+, K^+) in the presence of NaOH have been studied in DMF solution. In this case the ability of the dendrimer to detect the investigated metal cations has been tested in DMF solution by monitoring the changes in the absorption and fluorescent spectra. DMF has been chosen as a solvent for all the spectral measurements in the presence of metal cations since this solvent guarantees a good solubility of the dendrimer ligand, its complexes with metal cations and the respective metal salts as a source for the metal cations. The choice of DMF as an organic solvent for the spectral measurements was also due to the fact that the dendrimer under study can change its colour in the presence of hydroxyl ions. In this case, the changes in the colour and in the fluorescence intensity in the presence of the metal cations are of particular importance.

In pure DMF solution the hexylamino groups from the 1,8-naphthalimides at the dendrimer are not deprotonated, that is why it does not change its absorption and fluorescence spectral characteristics in the presence of alkali metal cations.

Therefore for practical applications, equivalent quantity of sodium hydroxide has been added to the dendrimer solution. After the colour change from yellow to red the metal cations were added. Fig. 3 shows the change in the absorption spectra after the titration with different amounts of Li^+. As seen the absorption of the maxima at 335 and 531 nm is lower while the one at 439 nm increases. The addition of Li^+ at a concentration of 3×10^{-5} mol l^{-1} causes no more changes in the absorption spectra. In this case the colour is changed from red to yellow.

Fig. 4 reveals the effect of Li^+ and Na^+ cations on the fluorescence intensity of the deprotonated dendrimer in DMF solution. In the presence of Li^+ (Fig. 4A) the fluorescence maximum undergoes a large shift of 88 nm. The position of fluorescence maximum is identical with the one assigned to the dendrimer in DMF solution without NaOH. The addition of Li^+ to the dendrimer solution up to 3×10^{-5} mol l^{-1} leads to a strong increase in the fluorescence intensity. In the presence of Li^+ a dramatic change of the colour and fluorescence intensity has been observed. Probably Li^+ first of all attacks the negative charge of the deprotonated nitrogen atom at C-4 position of the naphthalene ring which leads to its neutralization and restoration of the colour from red to yellow. The further rise in the fluorescence intensity with the increase of Li^+ concentration up to 3×10^{-5} mol l^{-1} is probably due to a coordination of Li^+ in the dendrimer core. After this concentration the increase in the fluorescence is negligible.

On the contrary, in the presence of Na^+ cations only the position of the fluorescence maximum is shifted (also with 88 nm) while the fluorescence remains negligible (Fig. 4B). The availability of Na^+ in the solution is responsible only for the neutralization of the negative charge, hence Na^+ does not form a stable complex with the dendrimer core as Li^+ cations do.

The enhancement of the fluorescence intensity (FE) for dendrimer solutions in the presence of metal cations can be evaluated by $FE = I/I_0$ where I/I_0 represents the ratio of the maximum of fluorescence intensity I (upon the addition of metal cations) and the minimum of fluorescence intensity I_0 (before the addition of metal cations). Fig. 5 shows the dependence of fluorescence enhancement as a function of the nature of metal cations. This figure shows

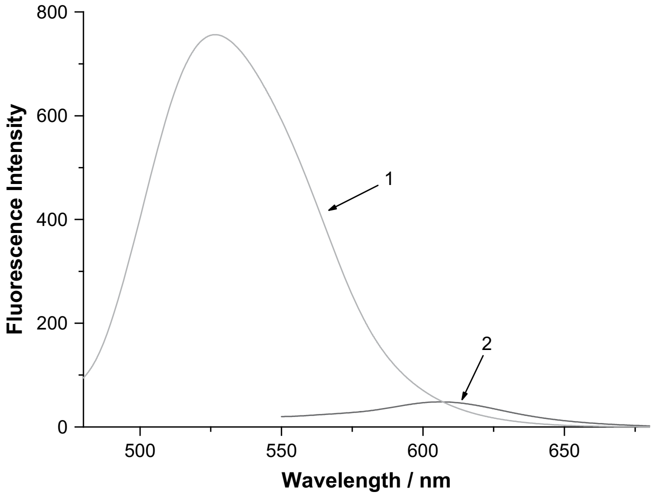

Fig. 2. Fluorescence spectra of the dendrimer ($c = 1 \times 10^{-6}$ mol l^{-1}) without, $\lambda_{Ext} = 439$ nm (1) and with NaOH ($c = 1.6 \times 10^{-5}$ mol l^{-1}) $\lambda_{Ext} = 531$ nm (2).

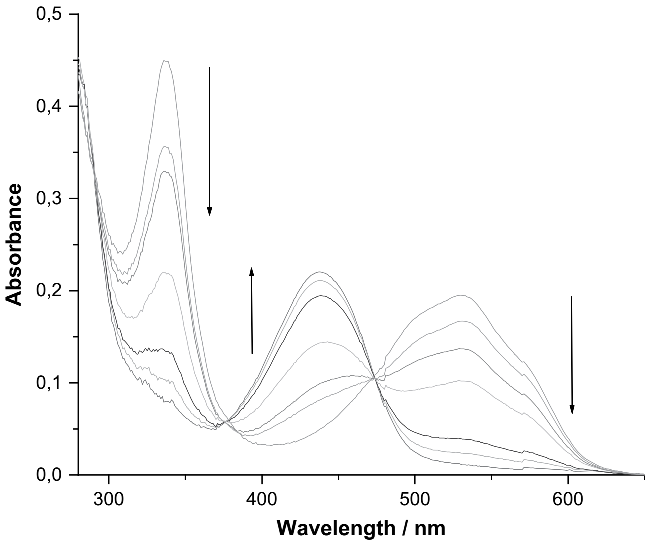

Fig. 3. Change of the absorption spectra of dendrimer + NaOH ($c = 1.6 \times 10^{-5}$ mol l^{-1}) in DMF solution upon addition of Li^+ cations ($c = 0–3 \times 10^{-5}$ mol l^{-1}). The concentration of dendrimer is 1×10^{-6} mol l^{-1}.

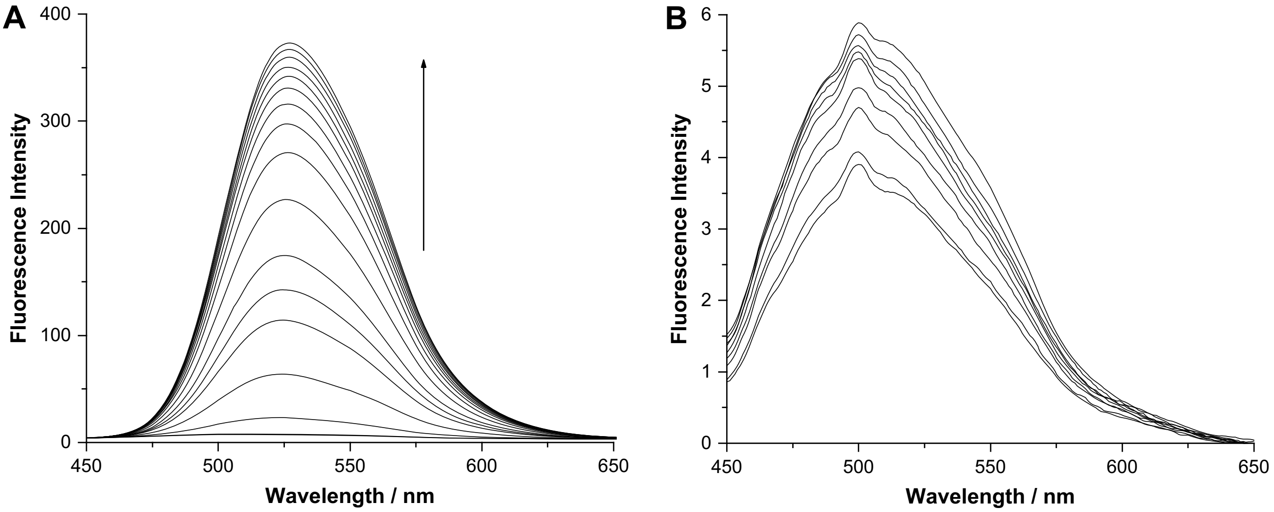

Fig. 4. Fluorescence spectra of dendrimer + NaOH ($c = 1.6 \times 10^{-5}$ mol l^{-1}) in DMF in different concentrations of metal cations ($c = 0$–3×10^{-5} mol l^{-1}). The concentration of dendrimer is 1×10^{-6} mol l^{-1}. (A – Li), (B – Na).

clearly that only the lithium cation possesses an important FE, and the dendrimer can be used as sensor for such cations.

The fluorescence spectrum of the dendrimer taken in the presence of metal cations (Na^+, K^+ and Li^+), each of them at a concentration of 3×10^{-5} mol l^{-1}, is presented in Fig. 6. The fluorescence intensity in the presence of both K^+ and Na^+ is slightly higher (FE = 1.2 and 1.6 respectively) than that of the solution free of the metal cations. The addition of Li^+ at a concentration of 3×10^{-5} mol l^{-1} to the same solution causes a drastic increase in fluorescence intensity (FE = 112). Most probably Li^+ is more competitive in the complex forming reaction of the dendrimer core. These data prove the high selectivity of the dendrimer and its high prospects to be used as a detector of Li^+ cations.

The basic photophysical characteristics of the dendrimer in DMF solution in the presence of all alkali metal cations under study are summarized in Table 2: absorption (λ_A) and fluorescence (λ_F) maxima, fluorescence enhancement (FE), Stokes shift ($\nu_A - \nu_F$), and quantum fluorescence yield (Φ_F). As seen from this table, whatever be the metal cation the absorption and fluorescence maxima are nearly the same in comparison with the values obtained for the dendrimer solution without any metal cations (see Table 1) which indicates an interaction between the dendrimer and the respective metal cations in the excited state. The data also show the higher quantum yield value obtained for Li^+ ($\Phi_F = 0.31$) in comparison with those obtained for either Na^+ or K

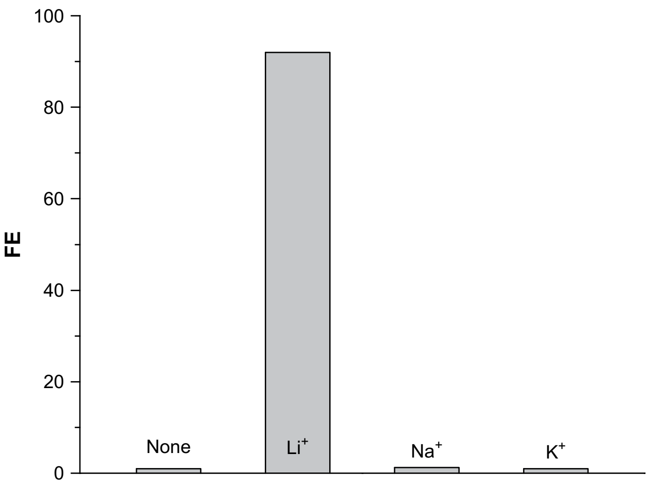

Fig. 5. Fluorescence enhancement factor (FE) of the dendrimer in the presence of different metal cations ($c = 3 \times 10^{-5}$ mol l^{-1}) in DMF + NaOH ($c = 1.6 \times 10^{-5}$ mol l^{-1}) solution. The dendrimer concentration in solution is $c = 1 \times 10^{-6}$ mol l^{-1}.

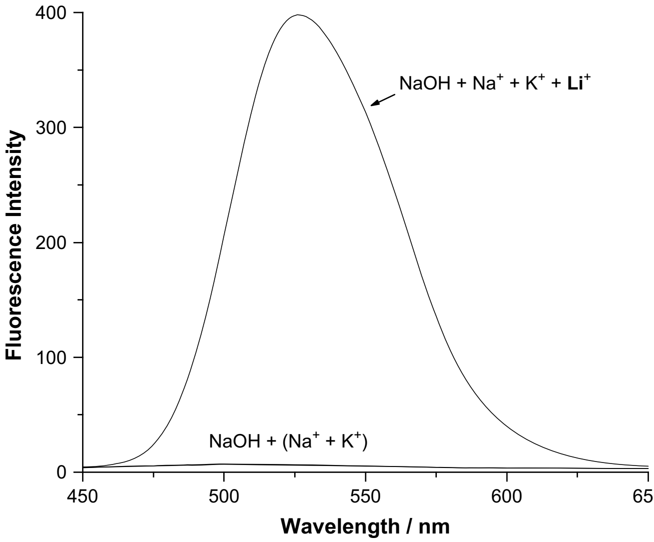

Fig. 6. Fluorescence spectra of the dendrimer ($c = 1 \times 10^{-6}$ mol l^{-1}) in DMF + NaOH in the presence of various metal cations. The concentrations of metal cations were 3×10^{-5} mol l^{-1}.

Table 1
Photophysical characteristics of the dendrimer in DMF solution and in the presence of NaOH ($c = 1.6 \times 10^{-5}$ mol l^{-1}).

Dendrimer	λ_A	ε	λ_F	$\nu_A - \nu_F$	Φ_F
	nm	l mol^{-1} cm^{-1}	nm	cm^{-1}	
D [7]	439	189,300	524	3695	0.32
D + OH$^-$	531	193,500	612	716	0.0006

Table 2
Photophysical characteristics of the dendrimer in DMF solution after its deprotonation in the presence of cations.

System	λ_A nm	λ_F nm	$\nu_A - \nu_F$ cm^{-1}	FE	Φ_F
$D + OH^- + Li^+$	439	528	3839	112	0.31
$D + OH^- + Na^+$	439	528	3839	1.6	0.0006
$D + OH^- + K^+$	438	527	3855	1.2	0.0006

($\Phi_F = 0.0006$) which is in agreement with the FE values obtained previously.

4. Conclusions

We have demonstrated that in DMF solution and in alkali media a PAMAM dendrimer modified with 4-hexylamino-1,8-naphthalimide units in its periphery changed drastically its photophysical properties. The change in the colour of the dendrimer solution from yellow to red and the significant bathochromic shifts of fluorescence have been attributed to the deprotonation of the hexylamino groups at C-4 position of the 1,8-naphthalimide structures. In alkali media the dendrimer can interact with all metal cations studied but coordinate only in the dendrimer core with Li^+ cations, exhibiting excellent selectivity over Na^+ and K^+ cations. The lowest concentration detected by the new sensor is 1×10^{-6}, the range spans up to 3×10^{-5} mol l^{-1} that reveals a good sensitivity and opens possibilities for applications when even small amounts of pollutants do matter. Sensors for these ions are widely studied. Though selective, colorimetric and ratiometric fluorescent sensors for Li^+ cations have not attracted the due attention and been discussed yet.

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